MEASUREMENT AND MODELING OF THE ALUMINA SOLUBILITY IN CRYOLITE MELTS AT 1300K

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The solubility of alumina in cryolite melts and the melt structure of the NaF-AlF_3-Al_2O_3 system, have been active subjects of study over a long period of time, mainly because of the industrial importance in connection with primary aluminum production by the Hall-Heroult process. The alumina solubility in cryolite melts with a composition range of $1.5 \leq$ cryolite ratio $r \leq 3$ was well determined experimentally. However, the solubility data of alumina in basic melts are not consistent. For the melt structure of NaF-AlF_3 with dissolved alumina, a number of models have been proposed, with different solutes involved. Therefore, further work was necessary to achieve an improved knowledge and correlation in the alumina solubility and the melt structure.

In this study, the solubility of alumina was measured experimentally in neutral and basic cryolite melts with a composition range of $3 \leq$ cryolite ratio $r \leq 12$. Thermodynamic activity probes for Al and for Na were used to monitor the melt basicity ($\log a_{NaF}$) and acidity ($\log a_{AlF_3}$) in the solubility measurements so that the solubility of alumina was described for the first time in terms of a quantitative measure of melt basicity. The experimentally determined alumina solubility indicates a maximum value at approximately $r = 4$ at 1300K, as shown in Fig. 1.

The newly measured alumina solubility data, combined with those well determined experimentally for the melts with a composition range of $1.5 \leq r \leq 3$, were used to model the melt structure of NaF-AlF_3-Al_2O_3 system. From the preliminary attempt, $Na_2Al_2OF_6$, $Na_2Al_2O_2F_4$ and $Na_4Al_2O_2F_6$ were assumed as acidic, neutral and basic oxyfluoride solutes in cryolite melts, respectively. Na_3AlF_6, Na_2AlF_5 and $NaAlF_4$ were considered as the oxygen-free solutes existing in the molten salts, with some NaF remaining in the melts. The molar fraction for each solute is related to its equilibrium constant and available activity data for NaF and AlF_3. From the element balances for oxygen, aluminum, sodium and fluorine, and from the sum of moles for all the solutes, a set of equations was created for different compositions (basicity) of melts, and solved for equilibrium constants using a computer software which provided a minimum overall error for all the relations.

According to the present model, the three solutes $Na_2Al_2OF_6$, $Na_2Al_2O_2F_4$ and $Na_4Al_2O_2F_6$ describe perfectly the melt structure of NaF-AlF_3 system with dissolved alumina, as shown in Fig. 1. The acidic solute $Na_2Al_2OF_6$ is the dominant species in an acidic melt with the cryolite ratio r close to 1.5; with the increase in the melt basicity the neutral solute $Na_2Al_2O_2F_4$ becomes more important than the other two solute complexes. In basic melts, a significant contribution to alumina solubility is provided from the basic solute $Na_4Al_2O_2F_6$. The 3-D geometries for all these three solutes are also proposed in the present study.

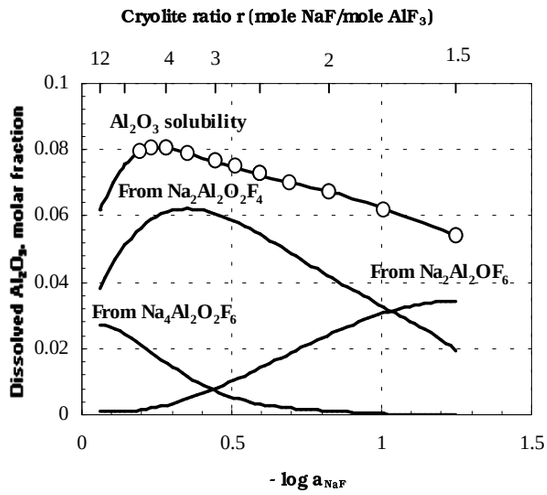

Fig. 1 Comparison of alumina solubility in NaF-AlF_3 system at 1300K as a function of melt basicity from experiments (data points) and calculated from the present model (top line). The other three lines represent the individual alumina solubility contribution by acidic ($Na_2Al_2OF_6$), neutral ($Na_2Al_2O_2F_4$) and basic ($Na_4Al_2O_2F_6$) solutes, respectively.